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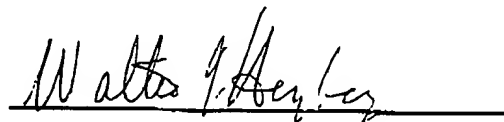
**VERIFICATION OF A TRANSLATION**

I, the below named translator, hereby declare as follows:

My name and post office address are as stated below.

I am knowledgeable in the English language and in the language of the attached foreign language document and I believe the attached English translation of that document, which has the title, "**COMPOSITION FOR DYEING FIBERS**", is a true and complete translation thereof.

All statements made herein of my own knowledge are true and all statements made on information and belief are believed to be true; and further these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 or Title 18 of the United States Code and that such willful false statements may jeopardize the validity of any decisions made, such as the granting of a patent, based on this translation.



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## COMPOSITION FOR DYEING FIBERS

The object of the present invention is a composition, containing aromatic enamines and carbonyl compounds, for dyeing fibers, particularly keratin fibers (such as human hair), a method for dyeing fibers, especially keratin fibers, a multi-component kit for dyeing and, later on, decolorizing fibers, particularly human hair, which kit contains a composition for producing a dyeing of the fibers as well as a composition for the reductive removal of the dyeing, as well as a method for dyeing and later on decolorizing fibers, particularly keratin fibers.

Hair dyeing compositions are divided mainly into the area of oxidation dyes and that of tinting, depending on the initial color of the hair that is to be dyed and on the end result desired. Oxidizing hair dyes are outstandingly suitable for covering larger portions of gray. Oxidizing dyeing agents, which are used when the gray portion does not exceed 50%, generally are referred to as oxidative tints, whereas the oxidizing dyeing agent, used when the gray portion exceeds 50% or for "brighter dyeing", usually are referred to as oxidative dyes. Direct dyes are contained mainly in non-oxidizing dyes (so-called tinting agents). Direct dyes are contained mainly in non-oxidative dyeing agents (so-called tinting agents). Because of their small size, some direct dyes, such as the nitro dyes, can penetrate into the hair and dye it directly, at least in the outer regions. Such tints treat the hair very gently and usually withstand 6 to 8 washings and enable gray to be covered to about 20% to be covered.

In general, direct and oxidative tints are washed out of the hair after a few washings. The time period depends very much on such factors as the structure of the hair and on the shade used. Oxidative dyes can partly fade with time, but usually remain in the hair until it is cut the next time. However, removal of the hair dyeing at

any time may be desirable if a particular color is to be worn only for a certain time or if the user is not satisfied with the dyeing. Likewise, when hair dyeing is used for the first time, the possibility of removing the dyeing gently and completely reduces the fear of too drastic a color change ("dyeing as a test").

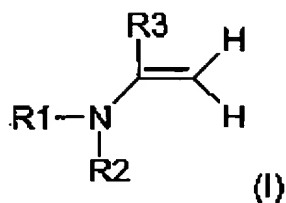
The German Offenlegungsschrift 197 45 292 discloses the use of a combination of malonaldehyde derivatives, such as malonaldehyde bis-dialkyl acetals, and amines or compounds with an acidic CH group for dyeing hair without the use of oxidizing agents. Likewise, it is known from the state of the art, for example, from K.H. Schrader, "Grundlagen und Rezepturen der Kosmetika (Fundamentals and formulations of cosmetics)", 2<sup>nd</sup> edition (1989), pages 807 and 808, that so-called stripping agents, which contain active reducing or oxidizing agents, can be used for removal of unsuccessful dyeings. However, such stripping agents cause considerably damage to the hair and remove the dye completely only in rare cases.

It is the task of the present invention to make a dyeing system available which, without the addition of oxidizing agents (such as hydrogen peroxide), lead on the one hand to a gentle, intensive and permanent dyeing of the fibers and, on the other, make possible a gentle and complete removal of this dyeing at any time.

Surprisingly, it has now been found that, by using a dyeing agent, obtained by mixing an enamine of formula (1) with a dyeing agent containing a carbonyl compound, intensive dyeings are achieved in a gentle manner and can be removed completely at any given later time.

The object of the present invention therefore is a composition for dyeing fibers (A), such as wool, silk, cotton or hair and, in particular, human hair, which is obtained by mixing two components and characterized in that the one

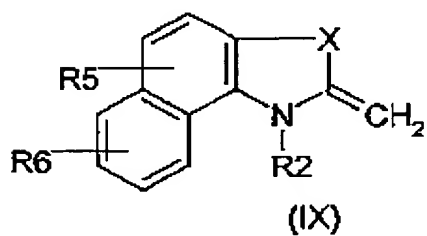
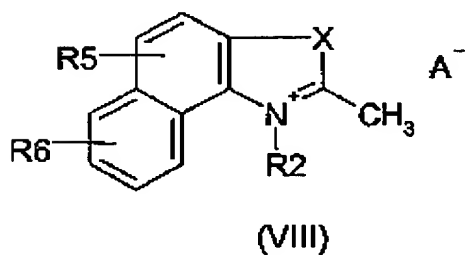
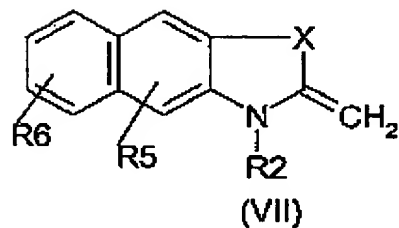
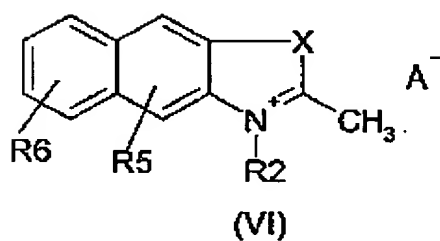
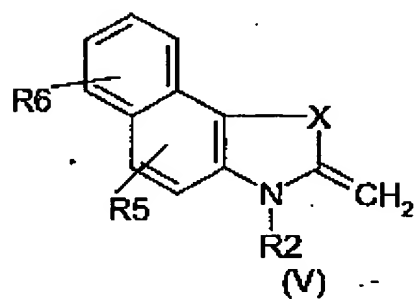
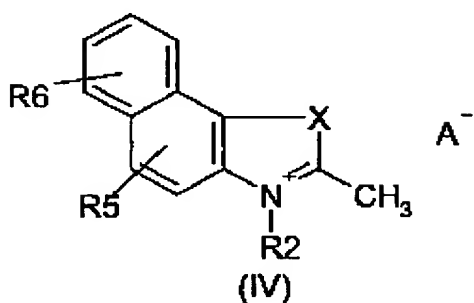
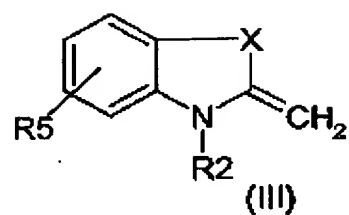
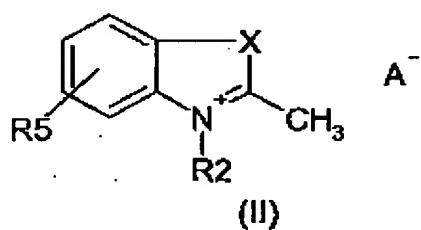
component (component A1) contains at least one enamine of formula (I) or its physiologically tolerated salt,



in which R1 is an aromatic group, with one or more aromatic rings, particularly a 5-membered or 6-membered aryl group, preferably a phenyl group, which is optionally substituted by a C1 to C4 alkyl group, a C1 to C4 hydroxyalkyl group, a hydroxy group, a methoxy group, a dialkylamino group or a halogen group or a 5-membered or a 6-membered heterocyclic group, preferably a pyridyl group, or a naphthyl group; R2 is a linear or branched C1 to C8 alkyl group, a linear or branched C1 to C8 hydroxyalkyl group or a C1 to C8 alkoxyalkyl group, there possibly being oxygen atoms between the carbon atoms of the alkyl chain, R3 is a linear or branched C1 to C8 alkyl group, a C1 to C8 alkoxyalkyl group or a linear or branched C1 to C8 alkylene group, a C1 to C8 alkoxyalkylene group, -O-, -NH-, -NR<sub>4</sub>- or -S- and R<sub>4</sub> is an alkyl group, an alkoxyalkyl group, a hydroxyalkyl group or hydrogen, the R1 and R3 groups, together with the nitrogen atom and the carbon atom of the basic enamine structure being able to form a cyclic compound and the other component (component A2) contains at least one carbonyl compound, particularly an aldehyde.

Preferred are compounds of formula (1), in which the R1 and R3 groups, together with the nitrogen atom and the carbon atom of the basic enamine structure, form a cyclic compound, R3 preferably being connected with the carbon atom of the aromatic R1 group that is in the position ortho to the enamine-substituted carbon atom.

Especially preferred are enamines of formulas (II) to (IX).



in which X is a carbon atom, which is substituted by two C1 to C4 alkyl groups (particularly by two methyl groups) or by a C1 to C4 alkyl group and a hydroxyl group, a sulfur atom, an alkylated or not alkylated nitrogen atom or an oxygen atom, and R2 is a linear or branched C1 to C8 alkyl group, a linear or branched C1 to C8

hydroxyalkyl group or a C1 to C8 alkoxyalkyl group, there possibly being oxygen atoms between the carbon atoms of the alkyl chain, R5 and R6, independently of one another, are hydrogen, a linear or branched C1 to C4 alkyl group, a linear or branched C1 to C4 hydroxyalkyl group, a hydroxy group, a methoxy group, an amino group, a dialkylamino group or a halogen atom, and A<sup>-</sup> is chloride, bromide, iodide, hydrogen sulfate, monomethyl sulfate, sulfate, hexafluorophosphate, hexafluoroantimonate, tetrafluoroborate, tetraphenyl borate and preferably chloride, bromide and hydrogen sulfate.

Of the compounds of formulas (I) to (IX), the following are particularly preferred: 3-ethyl-2-methylenebenzothiazolin, 2-methylene-1,3,3-trimethylindolin, 1,2,3,3-tetramethyl-3H-indolinium chloride, 1,2,3,3-tetramethyl-3H-indolinium bromide, 1,2,3,3-tetramethyl-3H-indolinium iodide, 1,2,3,3-tetramethyl-3H-indolinium sulfate, 1,2,3,3-tetramethyl-3H-indolinium hydrogen sulfate, 1,2,3,3-tetramethyl-3H-indolinium methyl sulfate, 1,2,3,3-tetramethyl-3H-indolinium hexafluorophosphates, 1,2,3,3-tetramethyl-3H-indolinium hexafluoroantimonate, 1,2,3,3-tetramethyl-3H-indolinium tetrafluoroborate, 5-chloro-2-methylene-1,3,3-trimethylindolin or its salts, 1-(2-hydroxyethyl)-3,3-dimethyl-2-methylene-indolin or its salts, 1,1,2,3-tetramethyl-1H-benz(e)indolinium chloride, 1,1,2,3-tetramethyl-1H-benz(e)indolinium bromide, 1,1,2,3-tetramethyl-1H-benz(e)indolinium iodide, 1,1,2,3-tetramethyl-1H-benz(e)indolinium sulfate, 1,1,2,3-tetramethyl-1H-benz(e)indolinium hexafluorophosphate, 1,1,2,3-tetramethyl-1H-benz(e)indolinium methyl sulfate, 1,1,2,3-tetramethyl-1H-benz(e)indolinium hexafluoroantimonate and 1,1,2,3-tetramethyl-1H-benz(e)indolinium tetrafluoroborate,

The following aldehyde, in particular, are named as suitable carbonyl compounds: vanillin (4-hydroxy-3-methoxybenzaldehyde), isovanillin (3-hydroxy-4-methoxybenzaldehyde), 3,4-dihydroxybenzaldehyde, 4-hydroxybenzaldehyde, 3,5-dimethoxy-4-hydroxybenzaldehyde, 4-dimethylaminobenzaldehyde, 4-methyl-5-imidazolcarboxaldehyde, 4-dimethylaminocinnamaldehyde, 4-hydroxy-2-methoxy-

benzaldehyde, 3,5-dimethyl-4-hydroxybenzaldehyde, 4-dimethylamino-2-methoxybenzaldehyde, 2-hydroxybenzaldehyde, 4-hydroxy-1-naphthaldehyde, 4-methoxy-1-naphthaldehyde, 4-dimethylamino-1-naphthaldehyde, 4'-hydroxybiphenyl-1-carbaldehyde, 2-hydroxy-3-methoxybenzaldehyde, 2,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 2,5-dihydroxybenzaldehyde, 2,3,4-trihydroxybenzaldehyde, 3,4,5-trihydroxybenzaldehyde, 2,4,6-trihydroxybenzaldehyde, 2,4-dimethoxybenzaldehyde, 2,3-dimethoxybenzaldehyde, 2,5-dimethoxybenzaldehyde, 3,5-dimethoxybenzaldehyde, 3,4-dimethoxybenzaldehyde, indole-3-carbaldehyde, benzene-1,4-dicarbaldehyde, 4-ethoxybenzaldehyde, 2-methyl-1,4-naphthoquinone, 4-carboxybenzaldehyde, 4-hydroxy-3-methoxycinnamaldehyde, 3,5-dimethoxy-4-hydroxy-cinnamaldehyde, 3-methoxy-4-(1-pyrrolidinyl)-benzaldehyde, 4-diethylamino-3-methoxybenzaldehyde, 1,2-phthaldehyde, pyrrole-2-aldehyde, thiophene-2-aldehyde, thiophene-3-aldehyde, chromone-3-carboxyaldehyde, 6-methyl-4-oxo-1(4H)-benzopyran-3-carbaldehyde, N-methylpyrrole-2-aldehyde, 5-methylfurfural, 6-hydroxychromene-3-carboxaldehyde, 6-methylindole-3-carboxaldehyde, 4-dibutylaminobenzaldehyde, N-ethylcarbazol-3-aldehyde, 4-diethylamino-2-hydroxybenzaldehyde, 3,4-dimethoxy-5-hydroxybenzaldehyde, 5-(4-(diethylamino)phenyl)-2,4-pentadienal, 2,3-thiophenedicarboxaldehyde, 2,5-thiophenedicarboxaldehyde, 2-methoxy-1-naphthaldehyde, 3-ethoxy-4-hydroxybenzaldehyde, 2-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-nitrobenzaldehyde.

The enamine and the carbonyl compound are kept separated from one another until shortly before use. As a rule, the inventive dyeing agent consists of a mixture of the two components A1 and A2, namely a dye composition (A1), which contains the enamine and optionally the direct dye, and a further dye composition (A2), which contains the carbonyl compound and optionally direct dyes. These two components are mixed immediately before use into a ready-for-use dyeing agent and then applied on the fibers, which are to be dyed. Of course, it is also possible that one

or more of the two components consists of several individual components, which are mixed with one another before use.

The enamines of formula (I) and the carbonyl compounds are contained in the respective dye composition (component A1 or component A2) in each case in a total amount of about 0.02 to 20 percent by weight and preferably of 0.2 to 10 percent by weight, the enamine of formula (I) and the carbonyl compound in each case being contained in a total amount of about 0.01 to 10 percent by weight and preferably of 0.1 to 5 percent by weight in the ready-for-use dyeing agent, which is obtained by mixing the components A1 and A2.

Furthermore, the inventive dyeing agent optionally may contain conventional, physiologically safe direct dyes from the group comprising the nitro dyes, azo dyes, quinone dyes and triphenylmethane dyes.

The direct dyes can be used in the component A1 and the component A2 in each case in a total amount of about 0.02 to 20 percent by weight and preferably of 0.2 to 10 percent by weight, the total amount of direct dyes being about 0.01 to 10 percent by weight and preferably 0.1 to 5 percent by weight in the ready-for-use dyeing agent obtained by mixing components A1 and A2.

The dyeing agent A and the components A1 and A2 can be prepared in the form, for example, of a solution, particularly of an aqueous or aqueous alcoholic solution. Further suitable forms of preparation are a cream, a gel, an aerosol foam or an emulsion. Their composition represents a mixture of the enamines of formula (I) and/or of the carbonyl compounds with the additives, which are customary for such preparations.

Conventional additives, used in dyeing agents in solutions, creams, emulsions, gels or aerosol foams are, for example, solvents such as water, low



molecular weight aliphatic alcohols, such as ethanol, n-propanol and isopropanol or glycols such as glycerin and 1,2-dihydroxypropane, furthermore wetting agents or emulsifiers from the class of anionic, cationic, amphoteric or nonionic surface active substances, such as fatty alcohol sulfates, ethoxylated fatty alcohol sulfates, alkyl sulfonates, alkylbenzene sulfonates, alkyltrimethylammonium salts, alkyl betaines, ethoxylated fatty alcohols, ethoxylated nonylphenols, fatty acid alkanolamides, ethoxylated fatty alcohols, ethoxylated nonylphenols, fatty acid alkanolamides, ethoxylated esters of fatty acids, furthermore thickeners such as higher molecular weight fatty alcohols, starch or cellulose derivatives, perfumes, hair pre-treatment agents, conditioners, hair swelling agents, preservatives, furthermore petrolatum, paraffin oil and fatty acids, as well as cosmetics, such as cationic resins, lanolin derivatives, cholesterol, pantothenic acid and betaine. The components mentioned are used in amounts, customary for such purposes; for example, the wetting agents and emulsifiers are used in concentrations of 0.5 to 30% by weight (based on the dye composition), the thickener is used in an amount of about 0.1 to 25% by weight (based on the dye composition) and the cosmetics are used in a concentration of about 0.1 to 5.0% by weight (based on the dye composition).

The pH of the ready-for-use dyeing agent A usually is 3 to 11 and preferably 6 to 11, the pH of the ready-for-use dyeing agent being adjusted during the mixing of the enamine-containing component A1, which preferably is alkaline, with the carbonyl-containing component A2, which preferably is acidic, to a value, which is affected by the amount of alkali in the component A1 and the amount of acid in the component A2, as well as by the ratio, in which these two components are mixed.

For adjusting the pH to the value desired for the dyeing, alkalizing agents, such as alkanolamines, alkylamines, alkali hydroxides or ammonium hydroxide and alkali carbonates or ammonium carbonate or acids such as lactic acid, acetic acid, tartaric acid, phosphoric acid, hydrochloric acid, citric acid, ascorbic acid and boric acid can be used.

The ready-for-use dyeing agent A is prepared immediately before use by mixing the enamine-containing component A1 with the component A2, which contains the carbonyl compound, and is then applied to the fibers. Depending on the depth of shade desired, this mixture is allowed to act for 5 to 60 minutes and preferably for 15 to 30 minutes at a temperature of 20 to 50 degrees centigrade and especially of 30 to 40 degrees centigrade. Subsequently, the fiber is rinsed with water and optionally washed with a shampoo.

The inventive dyeing agent A makes possible a gentle, uniform and permanent dyeing of the fibers, especially of keratin fibers, such as hair. Surprisingly, these dyeing can be decolorized completely once again rapidly and gently at any time by reducing agents.

A further object of the present invention therefore is a multi-component kit for dyeing and later decolorizing fibers, such as wool, silk, cotton or hair and especially human hair, wherein the kit contains the inventive dyeing agent A and a decolorizing component B, the latter, as the decolorizing agent, containing at least one sulfite, such as ammonium sulfite, alkali sulfite or alkaline earth sulfite, especially sodium sulfite or ammonium sulfite.

The total amount of sulfites in component B is about 0.1 to 10% by weight and preferably 2 to 5% by weight.

The agent for decolorizing the fibers, dyed with the dyeing agent A (referred to subsequently as "decolorizing agent") may be present as an aqueous or aqueous alcoholic solution, as a gel, a cream, an emulsion or a foam and can be produced in the form of a one-component preparation as well as in the form of a multi-component preparation. The decolorizing agent can be produced as a powder or, for protection against dust formation, also as a tablet - including an effervescent

tablet - or as a granulate. From this, with cold or warm water, optionally with the addition of one or more auxiliary materials named in the following, the decolorizing agent is produced before use. It is, however, also possible for these auxiliary materials, provided that they are solids, to be contained already in the decolorizing powder or the decolorizing granulate or the effervescent tablet. Dust formation can be reduced additionally by wetting the powders with oils or waxes.

The decolorizing agent may contain additional auxiliary materials, such as solvents such as water, low molecular weight aliphatic alcohols, such as ethanol, n-propanol and isopropanol, glycol ethers or glycols such as glycerin and, in particular, 1,2-dihydroxypropane, furthermore wetting agents or emulsifiers from the classes of anionic, cationic, amphoteric or nonionic surface active substances, such as fatty alcohol sulfates, ethoxylated fatty alcohol sulfates, alkyl sulfonates, alkylbenzene sulfonates, alkyltrimethylammonium salts, alkyl betaines, ethoxylated fatty alcohols, ethoxylated nonylphenols, fatty acid alkanolamides, ethoxylated fatty alcohols, ethoxylated nonylphenols, fatty acid alkanolamides, ethoxylated esters of fatty acids, furthermore thickeners such as higher molecular weight fatty alcohols, starch or cellulose derivatives, perfumes, hair pre-treatment agents, conditioners, hair swelling agents, preservatives, petrolatum, paraffin oil and fatty acids, as well as cosmetics, such as cationic resins, lanolin derivatives, cholesterol, pantothenic acid and betaine.

The pH of the decolorizing agent is about 3 to 8 and especially 4 to 7. If necessary, the desired pH can be achieved by the addition of suitable acids, such as  $\alpha$ -hydroxy carboxylic acids, such as lactic acid, tartaric acid, citric acid or malic acid, phosphoric acid, acetic acid, glycolic acid, salicylic acid, glutathione or gluconic lactone, or by the addition of alkalizing agents such as alkanolamines, alkylamines, alkali hydroxides, ammonium hydroxide, alkali carbonates, ammonium carbonates or alkali phosphates.

The period of action of the decolorizing agent depends on the dyeing that is to be decolorized and on the temperature (about 20 to 50 degrees centigrade) and is 5 to 60 minutes and, in particular, 15 to 60 minutes. The decolorizing process can be accelerated by supplying heat. At the end of the period of action of the decolorizing agent, the hair is rinsed with water and optionally washed with a shampoo.

Although component B is particularly suitable for decolorizing hair, especially human hair, dyed with dyeing agent A, it can also be used to decolorize either natural or synthetic fibers, such as cotton, wool, silk, viscose, nylon and cellulose acetate, which have been dyed with dyeing agent A.

The object of the invention is described in greater detail by the following examples, without being limited to these.

### Examples

#### **Examples 1.1 to 1.6: Hair Dyeing Agents**

##### **Enamine-Containing Component A1**

Enamine of formula (I)	Quantitative Data
(stabilized with $\alpha$ -tocopherol (vitamin E))	as in Table 1
cetyl stearyl alcohol	12.00 g
ethoxylated stearyl alcohol with	
20 moles of ethylene oxide in the molecule (Steareth-20)	1.40 g
isopropanol	20.0 g
water, fully desalinated	to 100.0 g

##### **Aldehyde-Containing Component A2**

aldehyde compound	Quantitative Date as in Table 1
direct dye	Quantitative Date as in Table 1
cetyl stearyl alcohol	3.06 g

sodium lauryl sulfate	0.34 g
lanolin alcohol	0.50 g
water, fully desalinated	to 100.0 g

Component A1 (5 g) is mixed with 5 g of component A2. The ready-for-use hair-dyeing agent obtained is applied on bleached hair and distributed uniformly with a brush. After the agent has been allowed to act for a period of 30 minutes at a temperature of 40°C, the hair is washed with a shampoo, then rinsed with lukewarm water and dried.

**Table 1: Dyeing Results**

No.	a) Enamine-Containing Component A1 b) Aldehyde-Containing Component A2	Shade After Dyeing	Measured Color Values		
			L	a	b
<b>1.1</b>	in a) 1,3,3-trimethyl-2-methylene-indolin, 2.0 g	intensive red	+83.30	-0.48	+10.40
	in (b) 4-hydroxy-3-methoxy-benzaldehyde, 1.76 g	after the dyeing	+25.32	+58.19	+12.67
<b>1.2</b>	in a) 1,3,3-trimethyl-2-methylene-indolin, 2.0 g	intensive orange	+83.30	-0.48	+10.40
	in (b) 4-hydroxybenzaldehyde, 1.43 g	after the dyeing	+44.34	+73.22	+42.70
<b>1.3</b>	in a) 1,3,3-trimethyl-2-methylene-indolin, 2.0 g	intensive yellow	+83.3	-0.48	+10.40
	in b) 3-hydroxy-4-methoxybenzaldehyde, 1.76 g	after the dyeing	+58.96	+33.01	+66.62

Table 1 (Continuation)

No.	a) Enamine-Containing Component A1	b) Aldehyde-Containing Component A2	Shade After Dyeing	Measured Color Values		
				L	a	b
1.4	in a) 1,3,3-trimethyl-2-methylene-indolin, 2.0 g		intensive pink	+83.30	-0.48	+10.40
			untreated hair			
	in b) 4-dimethylaminobenzaldehyde 1.72 g		after the dyeing	+45.75	+77.26	+0.54
1.5	in a) 1,3,3-trimethyl-2-methylene-indolin, 2.0 g		intensive	+83.30	-0.48	+10.40
			wine-red			
	in b) 3,4-dihydroxybenzaldehyde 1.59 g		after the dyeing	+21.81	+37.19	+5.12

Table 1 (Continuation)

No.	a) Enamine-Containing Component A1	b) Aldehyde-Containing Component A2	Shade After Dyeing	Measured Color Values		
				L	a	b
1.6	in a) 1,3,3-trimethyl-2-methylene-indolin,		untreated hair	+83.30	-6.48	+10.40
	2.0 g		intensive red			
			brown			
	in b) 3,4-dihydroxybenzaldehyde					
	0.80 g					
	3-hydroxy-4-methoxybenzaldehyde					
	0.88g					
	1-(2-hydroxyethyl)amino-2-nitro-4-(di(-2-					
	hydroxyethyl)aminobenzene					
	(HC Blue No. 2) 2.00g		after the dyeing	+19.86	+16.36	3.51



**Examples 1.7 to 1.21: Hair Dyeing Agents**

**Component A1 Containing Enamine of Formula (I)**

enamine of Formula (I)	Quantitative Data as in Table 1
6-O-palmitoyl-L-ascorbic acid	0.30 g
cetyl stearyl alcohol	12.00 g
lauryl ether sulfate, 28%	10.00g
ethanol	23.00 g
water, fully desalinated	to 100.00 g

The cetyl stearyl alcohol is melted at 80°C. The lauryl ether sulfate is heated with 95% of the water to 80°C, added to the molten cetyl stearyl alcohol and stirred until a cream results. At room temperature, compound (I) is mixed with the remaining water, the alcohol and the 6-O-palmitoyl-L-ascorbic acid and then added. The pH of the cream is adjusted with 10% aqueous NaOH to a value of 12.0.

**Aldehyde-Containing Component A2**

aldehyde compound	Quantitative Data as in Table 1
direct dye	Quantitative Data as in Table 1
cetyl stearyl alcohol	12.00 g
lauryl ether sulfate, 28%	10.00 g
ethanol	23.00 g
water, fully desalinated	to 100.00 g

The cetyl stearyl alcohol is melted at 80°C. The lauryl ether sulfate is heated with 95% of the water to 80°C, added to the molten cetyl stearyl alcohol and stirred until a cream results. At room temperature, the aldehyde compound, as well as optionally the direct dyes, mixed with the remaining water and the alcohol, are added. The pH of the cream is adjusted with 10% aqueous lactic acid to a value of 4.0.

Component A1 (5 g) is mixed with 5 g of component A2. The ready-for-use hair-dyeing agent obtained is applied on bleached hair and distributed uniformly with a brush. After the agent has been allowed to act for a period of 30 minutes at a temperature of 40°C, the hair is washed with a shampoo, then rinsed with lukewarm water and dried.

The dyeings obtained are summarized in the following Table 2.

Table 2: Dyeing Results

No.	a) Enamine-Containing Component A1 b) Aldehyde-Containing Component A2	Shade After Dyeing	Measured Color Values		
			L	a	b
1.7	in (a) 1,1,2,3-tetramethyl-1H-benz(e)-indolinium chloride, 2.99 g	pink-red	+83.30	-0.48	+10.40
	in (b) 4-hydroxy-3-methoxybenzaldehyde, 1.76 g	untreated hair after the dyeing	+47.43	+50.09	+3.75
1.8	in (a) 1,1,2,3-tetramethyl-1H-benz(e)-indolinium bromide, 3.51 g	orange	+83.30	-0.48	+10.40
	in (b) 4-hydroxybenzaldehyde, 1.43 g	after the dyeing	+60.27	+53.71	+43.96
1.9	in (a) 1,1,2,3-tetramethyl-1H-benz(e)-indolinium chloride, 2.99 g	yellow	+83.30	-0.48	+10.40
	in (b) 3-hydroxy-4-methoxybenzaldehyde 1.76 g	after the dyeing	+68.20	+22.52	+57.04

Table 2: (continuation)

No.	a) Enamine-Containing Component A1 b) Aldehyde-Containing Component A2	Shade After Dyeing	Measured Color Values		
			L	a	b
<b>1.10</b>	in a) 1,1,2,3-tetramethyl-1H-benz(e)-	pink	+83.30	-0.48	+10.40
	indolinium methyl sulfate, 3.86 g in b) 4-dimethylaminobenzaldehyde 1,72 g	untreated hair after the dyeing	+52.30	+47.22	-7.93
<b>1.11</b>	in a) 1,1,2,3-tetramethyl-1H-benz(e)-	wine-red	+83.30	-0.48	+10.40
	indolinium bromide, 3.51 g in b) 3,4-dihydroxybenzaldehyde 1.59 g	untreated hair after the dyeing	+32.40	+37.51	+1.86
<b>1.12</b>	in a) 1,1,2,3-tetramethyl-1H-benz(e)-	blue-violet	+83.30	-0.48	+10.40
	indolinium iodide, 4.05 g in b) 3,5-dimethoxy-4-hydroxy benzaldehyde, 2.10 g	untreated hair after the dyeing	+36.10	+32.89	-17.69

Table 2: (continuation)

No.	a) Enamine-Containing Component A1 b) Aldehyde-Containing Component A2	Shade After Dyeing	Measured Color Values		
			L	a	b
1.13	in a) 1,1,2,3-tetramethyl-1H-benz(e)-indolinium chloride 2.99 g	petrol	+83.30	-0.48	+10.40
	in b) 3,4,5-trihydroxybenzaldehyde monohydrate, 1.98 g	untreated hair after the dyeing	+21.51	+11.82	-6.08
1.14	in a) 1,1,2,3-tetramethyl-1H-benz(e)-indolinium chloride, 3.00 g	violet	+83.30	-0.48	+10.40
	in b) 3,4-dihydroxybenzaldehyde, 0.80 g	untreated hair after the dyeing	+21.43	+11.30	-6.36
	3-hydroxy-4-methoxybenzaldehyde, 0.88 g				
	1-(2-hydroxyethyl)amino-2-nitro-4-(di(2-hydroxyethyl)amino)benzene (HC Blue No. 2). 2,00 g				

Table 2: (continuation)

No.	a) Enamine-Containing Component A1 b) Enamine-Containing Component A2	Shade After Dyeing		Measured Color Values		
				L	a	b
<b>1.15</b>	a) 1,2,3,3-tetramethyl-3H-indolinium chloride 2.42 g	intensive red	untreated hair	+83.30	-0.48	+10.40
	b) 4-hydroxy-3-methoxy benzaldehyde 1.76 g		after the dyeing	+25.32	+58.19	+12.67
<b>1.16</b>	a) 1,2,3,3-tetramethyl-3H-indolinium chloride 2.42 g	intensive orange	untreated hair	+83.30	-0.48	+10.40
	b) 4-hydroxybenzaldehyde, 1.43 g		after the dyeing	+44.34	+73.22	+42.70
<b>1.17</b>	a) 1,2,3,3-tetramethyl-3H-indolinium chloride, 2.42 g	intensive yellow	untreated hair	+83.30	-0.48	+10.40
	b) 3-hydroxy-4-methoxybenzaldehyde 1.76 g		after the dyeing	+58.96	+33.01	+66.62

Table 2: (continuation)

No.	a) Enamine-Containing Component A1 b) Enamine-Containing Component A2	Shade After Dyeing	Measured Color Values		
			L	a	b
1.18	a) 1,2,3,3-tetramethyl-3H-indolinium chloride 2.42 g	intensive pink	+83.30	-0.48	+10.40
	b) 4-dimethylaminobenzaldehyde	after the dyeing	+45.75	+77.26	+0.54
	1.72 g				
1.19	a) 1,2,3,3-tetramethyl-3H-indolinium chloride 2.42 g	intensive	+83.30	-0.48	+10.40
	b) 3,4-dihydroxybenzaldehyde	wine-red	+21.81	+37.19	+5.12
	1.59 g				
1.20	a) 1,2,3,3-tetramethyl-3H-indolinium chloride 2.42 g	intensive violet	+83.30	-0.48	+10.40
	b) 3,5-dimethoxy-4-hydroxybenzaldehyde	after the dyeing	+24.02	+49.64	-8.16
	2.10 g				

Table 2: (continuation)

No.	a) Enamine-Containing Component A1 b) Enamine-Containing Component A2	Shade After Dyeing	Measured Color Values		
			L	a	b
1.21	a) 1,2,3,3-tetramethyl-3H-indolinium bromide, 2.93 g	intensive	+83.30	-0.48	+10.40
		red-brown			
	b) 3,4-dihydroxybenzaldehyde 0.80g		+19.86	+16.36	+3..51
	3-hydroxy-4-methoxybenzaldehyde 0.88 g				
	1-(2-hydroxyethyl)amino-2-nitro-4-(di(2- hydroxyethyl)amino)benzene (HC Blue No. 2), 2.00 g	after the dyeing			



**Examples 2.1 to 2.20: Hair Dyeing Agents**

**Component A1 Containing Enamine**

enamine of Formula (I)	Quantitative Data as in Table 1
6-O-palmitoyl-L-ascorbic acid	0.30 g
cetyl stearyl alcohol	12.00 g
lauryl ether sulfate, 28% aqueous solution	10.00g
ethanol	23.00 g
water, fully desalinated	to 100.00 g

The cetyl stearyl alcohol is melted at 80°C. The lauryl ether sulfate is heated with 95% of the water to 80°C, added to the molten cetyl stearyl alcohol and stirred until a cream results. At room temperature, compound (I) is mixed with the ethanol/ the remaining water and the 6-O-palmitoyl-L-ascorbic acid, and then added. The pH of the cream is adjusted with 10% NaOH solution to a value of 11.0.

**Aldehyde-Containing Component A2**

aldehyde compound	Quantitative Data as in Table 1
cetyl stearyl alcohol	12.00 g
lauryl ether sulfate, 28% aqueous solution	10.00 g
6-O-palmitoyl-L-ascorbic acid	0.30 g
ethanol	23.0 g
water, fully desalinated	to 100.00 g

The cetyl stearyl alcohol is melted at 80°C. The lauryl ether sulfate is heated with 95% of the water to 80°C, added to the molten cetyl stearyl alcohol and stirred until a cream results. At room temperature, the aldehyde, mixed with the ethanol and the remaining water as well as the 6-O-palmitoyl-L-ascorbic acid, is added. The pH of the cream is adjusted with 10% aqueous lactic acid to a value of 4.0.

Component A1 and component A2 are mixed in a ratio of 1 : 1. The ready-for-use hair-dyeing agent, so obtained, is applied on the hair and distributed uniformly with a brush. After the agent has been allowed to act for a period of 30 minutes at a temperature of 40°C, the hair is washed with a shampoo, then rinsed with lukewarm water and dried.

The hair can be decolorized once again completely at 40°C at any time (for example, after several days or weeks) within a period of 20 minutes with a 5% sodium sulfite solution with a pH of 5 (component B).

The dyeing and decolorizing results obtained are summarized in the following Table.

Table 3:

No.	Enamine (1) Contained in A1 Aldehyde contained in A2	Shade After Dyeing	Measured Color Values			Degree of Decolorization (%)
			L	a	b	
<b>2.1</b>	in (A1) 1,2,3,3-tetramethyl-3H-indolinium chloride,	intensive	+83.30	-0.48	+10.40	
	2.42 g	red	+34.04	+68.92	+19.11	
	in (A2) 4-hydroxy-3-methoxybenzaldehyde, 1.76 g		+84.19	+9.28	+18.85	86
<b>2.2</b>	in (A1) 1,2,3,3-tetramethyl-3H-indolinium chloride,	intensive	+83.30	-0.48	+10.40	
	2.42 g	orange	+52.07	+69.44	+56.39	
	in (A2) 4-hydroxybenzaldehyde, 1.43 g		+82.72	11.60	+17.04	86
<b>2.3</b>	in (A1) 1,2,3,3-tetramethyl-3H-indolinium chloride,	intensive	+83.30	-0.48	+10.40	
	2.42 g	yellow	+67.01	+26.58	+78.16	
	in (A2) 3-hydroxy-4-methoxybenzaldehyde, 1.76 g		+84.10	+10.52	+17.29	84

Table 3: (continuation)

No.	Enamine (1) Contained in A1 Aldehyde contained in A2	Shade After Dyeing	Measured Color Values			Degree of Decolorization (%)
			L	a	b	
2.4	in (A1) 1,2,3,3-tetramethyl-3H-indolinium chloride, 2.42 g	intensive	+83.30	-0.48	+10.40	
		violet	+26.06	+52.34	-6.83	
		after the decolorizing	+80.48	+7.83	+15.56	88
2.5	in (A1) 2-methylene-1,3,3-trimethylindolin, 2.00 g in (A2) 3,4-dihydroxybenzaldehyde, 1.59 g	intensive	+83.30	-0.48	+10.40	
		wine-red	+24.17	+41.98	+8.34	
		after the decolorizing	+80.6	+9.09	+19.41	82
2.6	in (A1) 1,2,3,3-tetramethyl-1H-benz(e)indolinium iodide, 4.05 g in (A2) 3,5-dimethoxy-4-hydroxybenzaldehyde, 1.59 g	black	+83.30	-0.48	+10.40	
		after the dyeing	+23.05	+7.19	+0.35	
		after the decolorizing	30.81	+8.26	+12.45	85

Table 3: (continuation)

No.	Enamine (1) Contained in A1		Shade After Dyeing	Measured Color Values		
	Aldehyde contained in A2			L	a	b
2.7	in (A1) 1,1,2,3-tetramethyl-1H-		untreated hair	+83.30	-0.48	+10.40
	benz(e)indolinium chloride	red	after the dyeing	+47.43	+50.09	+3.75
	2.99 g					
	in (A2) 4-hydroxy-3-methoxy-	after the				
2.8	benzaldehyde, 1.76 g	decolorizing	white			
	in (A1) 1,1,2,3-tetramethyl-1H-	orange	untreated hair	+83.30	-0.48	+10.40
	benz(e)indolinium chloride		after the dyeing	+60.27	+53.71	+43.96
	2.99 g					
	in (A2) 4-hydroxybenzaldehyde	after the				
	1.43 g	decolorizing	white			

Table 3: (continuation)

No.	Enamine (1) Contained in A1		Shade After Dyeing	Measured Color Values		
	Aldehyde contained in A2			L	a	b
2.9	in (A1) 1,1,2,3-tetramethyl-1H-	yellow	untreated hair	+83.30	-0.48	+10.40
	benz(e)indolinium iodide,	after the	after the dyeing	+68.20	+22.52	+57.04
	4.05 g	decolorizing				
	in (A2) 3-hydroxy-4-methoxy- benzaldehyde 1.76 g		white			
2.10	in (A1) 1,1,2,3-tetramethyl-1H-	pink	untreated hair	+83.30	-0.48	+10.40
	benz(e)indolinium bromide,		after the dyeing	+52.30	+47.22	-7.93
	3.51 g	after the				
	in (A2) 4-dimethylamino- benzaldehyde, 1.72 g	decolorizing	white			

Table 3: (continuation)

No.	Enamine (1) Contained in A1		Shade After Dyeing	Measured Color Values		
	Aldehyde contained in A2	1H-		L	a	b
<b>2.11</b>	in (A1) 1,1,2,3-tetramethyl-	1H-	wine-red	+83.30	-0.48	+10.40
	benz(e)indolinium chloride,		untreated hair			
	2.99 g		after the dyeing	+32.40	+37.51	+1.86
	in (A2) 3,4-dihydroxy-		after the decolorizing			
<b>2.12</b>	benzaldehyde, 1.59 g		white			
	in (A1) 1,1,2,3-tetramethyl-	1H-	blue-violet	+83.30	-0.48	+10.40
	benz(e)indolinium chloride,		untreated hair			
	2.99 g		after the dyeing	+36.10	+32.89	-17.69
	in (A2) 3,5-dimethoxy-4-		after the decolorizing			
	hydroxybenzaldehyde, 2.10 g		white			

Table 3: (continuation)

No.	Enamine (1) Contained in A1		Shade After Dyeing	Measured Color Values		
	Aldehyde contained in A2			L	a	b
2.13	in (A1) 1,2,3,3-tetramethyl-3H-	intensive	untreated hair	+83.30	-0.48	+10.40
	indolinium chloride, 2.42 g	yellow	after the dyeing	+81.27	-4.04	+94.57
	in (A2) 4-methylimidazol-5-carboxaldehyde, 1.27 g	after the decolorizing	white			
2.14	in (A1) 1,2,3,3-tetramethyl-3H-	intensive	untreated hair	+83.30	-0.48	+10.40
	indolinium chloride, 2.42 g	yellow	after the dyeing	+47.00	+71.71	+47.92
	in (A2) 4-hydroxy-2-methoxybenzaldehyde, 1.75 g	after the decolorizing	white			



Table 3: (continuation)

No.	Enamine (1) Contained in A1		Shade After Dyeing	Measured Color Values		
	Aldehyde contained in A2			L	a	b
2.15	in (A1) 1,2,3,3-tetramethyl-3H-indolinium chloride, 2.42 g	intensive red	untreated hair	+83.30	-0.48	+10.40
			after the dyeing	+39.51	+72.92	+24.40
	in (A2) 3,5-dimethyl-4-hydroxybenzaldehyde, 1.73 g	after the decolorizing	white			
2.16	in (A1) 1,2,3,3-tetramethyl-3H-indolinium chloride, 2.42 g	intensive pink	untreated hair	+83.30	-0.48	+10.40
			after the dyeing	+37.36	+76.29	+6.25
	in (A2) 4-dimethylamino-2-methoxybenzaldehyde, 2.10 g	after the decolorizing	slightly pink			

Table 3: (continuation)

No.	Enamine (1) Contained in		Shade After Dyeing	Measured Color Values		
	Aldehyde contained in A2	A1		L	a	b
<b>2.17</b>	in (A1) 1,2,3,3-tetramethyl-3H-indolinium chloride, 2.42 g	intensive	untreated hair	+83.30	-0.48	+10.40
	in (A2) 3,4,5-trihydroxy-benzaldehyde, 2.0 g	red-violet after the decolorizing	after the dyeing	+19.53	+21.90	-2.69
<b>2.18</b>	in (A1) 1,2,3,3-tetramethyl-1H-benz(e)-indolinium chloride, 2.99 g	blue	untreated hair	+83.30	-0.48	+10.40
	in (A2) 3,4,5-trihydroxy-benzaldehyde, 2.0 g	after the decolorizing	after the dyeing	+21.51	+11.82	-6.08

Table 3: (continuation)

No.	Enamine (1) Contained in A1		Shade After Dyeing	Measured Color Values		
	Aldehyde contained in A2			L	a	b
2.19	in (A1) 5-chloro-2-methylene-	wine-red	untreated hair	+83.30	-0.48	+10.40
	1,3,3-trimethylindolin, 3.36 g		after the dyeing	+26.67	+45.74	-4.84
	in (A2) 3,4-dihydroxy-	after the				
2.20	benzaldehyde, 1.59 g	decolorizing	white			
	in (A1) 5-chloro-2-methylene-	orange	untreated hair	+83.30	-0.48	+10.40
	1,3,3-trimethylindolin, 3.36 g		after the dyeing	+54.25	+67.96	+39.02
	in (A2) 4-hydroxy-	after the				
	benzaldehyde, 1.43 g	decolorizing	white			

### **Examples 3.1 to 3.2: Hair Dyeing Agents**

#### **Enamine-Containing Component A1**

1,3,3-trimethyl-2-methylene-indolin	2.0 g
cetyl stearyl alcohol	12.0g
ethoxylated stearyl alcohol with	
20 moles of ethylene oxide in the molecule (Steareth 20)	1.40 g
isopropanol	20.0 g
water, fully desalinated	to 100.0 g

#### **Aldehyde-Containing Component A2 (3.1)**

4-hydroxy-3-methoxybenzaldehyde	1.76 g
cetyl stearyl alcohol	12.0g
ethoxylated stearyl alcohol with	
20 moles of ethylene oxide in the molecule(Steareth 20)	1.40 g
isopropanol	20.0 g
water, fully desalinated	to 100.0 g

#### **Aldehyde-Containing Component A2 (3.1)**

4-hydroxybenzaldehyde	1.41 g
cetyl stearyl alcohol	12.0g
ethoxylated stearyl alcohol with	
20 moles of ethylene oxide in the molecule(Steareth 20)	1.40 g
isopropanol	20.0 g
water, fully desalinated	to 100.0 g

Component A1 (5 g) is mixed with 5 g of component (A2 3.1 or A2 3.2), which contains the aldehyde. The ready-for-use hair-dyeing agent obtained is applied on bleached light-brown hair and distributed uniformly with a brush. After the agent has been allowed to act for a period of 30 minutes at a temperature of 40°C, the hair is rinsed with lukewarm water and then dried.

### **Examples 3.3 to 3.4 Hair Dyeing Agent**

**Enamine-Containing Component A1**

1,2,3,3-tetramethyl-3H-indolinium chloride	2.42 g
6-O-palmitoyl-L-ascorbic acid	0.30 g
cetyl stearyl alcohol	12.0g
lauryl ether sulfate, 28%	10.0 g
ethanol	23.0 g
water, fully desalinated	to 100.0 g

The cetyl stearyl alcohol is melted at 80°C. The lauryl ether sulfate is heated with 95% of the water to 80°C, added to the molten cetyl stearyl alcohol and stirred until a cream results. At room temperature, the 1,2,3,3-tetramethyl-3H-indolinium chloride is mixed with the remaining water and the alcohol and mixed with the 6-O-palmitoyl-L-ascorbic acid. The pH of the cream is adjusted with 10% aqueous NaOH to a value of 12.0.

**Aldehyde-Containing Component A2 (3.3)**

4-hydroxy-3-methoxybenzaldehyde	1.76 g
cetyl stearyl alcohol	12.0g
lauryl ether sulfate, 28%	10.0 g
ethanol	23.0 g
water, fully desalinated	to 100.0 g

**Aldehyde-Containing Component A2 (3.4)**

4-hydroxybenzaldehyde	1.416 g
cetyl stearyl alcohol	12.00 g
lauryl ether sulfate, 28%	10.00 g
ethanol	23.0 g
water, fully desalinated	to 100.0 g

The cetyl stearyl alcohol is melted at 80°C. The lauryl ether sulfate is heated with 95% of the water to 80°C, added to the molten cetyl stearyl alcohol and stirred until a cream results. At room temperature, the aldehyde, mixed with the remaining water and the alcohol, is added. The pH of the cream (A2/3.3) or (A2/3.4) is adjusted with 10% aqueous lactic acid to a value of 4.0.

Component A1 (5 g), containing the 1,2,3,3-tetramethyl-3H-indolinium chloride, is mixed with 5 g of the aldehyde-containing component (A2/3.3) or A2/3.4). The ready-for-use hair-dyeing agent obtained is applied on bleached light-brown hair and distributed uniformly with a brush. After the agent has been allowed to act for a period of 30 minutes at a temperature of 40°C, the hair is rinsed with lukewarm water and then dried.

During the subsequent washing test, the dyed strands are washed in each case 5 times with a shampoo, rinsed with water and dried. After each washing process, the L\*a\*b values are determined. The results are summarized in Table 4.

Table 4: Dyeing Results and Washing Stability

No.	Enamine (1) Contained in A1 Aldehyde contained in A2	Shade After Dyeing	Measured Color Values		
			L	a	b
3.1	in A1: 1,3,3-trimethyl-2-methylene-indolin in A2: 4-hydroxy-3-methoxy-benzaldehyde, 1.76 g	intensive red	60.31	+11.53	+31.63
		before the dyeing			
		after dyeing	27.60	+49.86	+7.56
		after 1 wash	28.44	+49.48	+6.63
		after 2 washes	28.24	+49.14	+5.55
		after 3 washes	28.66	+49.78	+5.47
		after 4 washes	28.27	+49.25	+6.39
		after 5 washes	28.16	+49.15	+6.34

Table 4: (continuation)

No.	Enamine (1) Contained in A1 Aldehyde contained in A2	Shade After Dyeing	Measured Color Values		
			L	a	b
3.2	in A1: 1,3,3-trimethyl-2-methyleneindolin, 2.0 g	intensive	60.31	+11.53	+31.63
		orange			
	in A2: 4-hydroxybenzaldehyde 1.41 g	After the dyeing	40.74	+55.06	+34.51
		after 1 wash	39.86	+54.07	+31.17
		after 2 washes	39.54	+53.48	+29.91
		after 3 washes	40.54	+53.43	+31.95
		after 4 washes	39.39	+52.29	+28.72
		after 5 washes	39.75	+51.24	+29.67



Table 4: Dyeing Results and Washing Stability

No.	Enamine (1) Contained in A1 Aldehyde contained in A2	Shade After Dyeing	Measured Color Values		
			L	a	b
3.3	in A1: 1,2,3,3-tetramethyl-3H-indolinium chloride, 2.42 g in A2: 4-hydroxy-3-methoxy-benzaldehyde, 1.76 g	intensive red	60.31	+11.53	+31.63
		before the dyeing			
		after the dyeing	27.60	+49.86	+7.56
		after 1 wash	28.44	+49.48	+6.63
		after 2 washes	28.24	+49.14	+5.55
		after 3 washes	28.66	+49.78	+5.47
		after 4 washes	28.27	+49.25	+6.39
		after 5 washes	28.16	49.15	+6.34

Table 4: Dyeing Results and Washing Stability

No.	Enamine (1) Contained in A1 Aldehyde contained in A2	Shade After Dyeing	Measured Color Values		
			L	a	b
3.4	in A1: 1,2,3,3-tetramethyl-3H-indolinium chloride, 2,42 g in A2: 4-hydroxybenzaldehyde 1.41 g	intense orange	60.31	11.53	31.63
		before the dyeing			
		after the dyeing	40.74	+55.06	+34.51
		after 1 wash	39.86	+54.07	+31.17
		after 2 washes	39.54	+53.48	+29.91
		after 3 washes	40.54	+53.43	+31.95
		after 4 washes	39.39	+52.29	+28.72
		after 5 washes	39.75	+51.24	+29.67

The L\*a\*b color values, given in the present examples, were measured with a Minolta Chromameter II color measuring device.

The L value here stands for the brightness (that is, the lower the L value, the greater is the color intensity), whereas the "a" value is a measure of the red portion (that is, the higher the "a" value, the greater is the red portion). The b value is a measure of the blue portion of the color and the more negative the b value, the greater is the blue portion.

The D value indicates the color difference, which exists between the untreated strands and the dyed or decolorized strands. It is determined from

$$D = \sqrt{(L_i - L_0)^2 + (a_i - a_0)^2 + (b_i - b_0)^2}$$

in which  $L_0$ ,  $a_0$  and  $b_0$  are the measured color values of untreated hair and  $L_i$ ,  $a_i$  and  $b_i$  are the values of the treated hair. The decolorization rate in percent was determined as follows:

$$\text{decolorization \%} = (1 - (D \text{ after decolorization} / D \text{ after dyeing})) \times 100$$

Unless stated otherwise, the percentages in the present application represent percentages by weight.